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**PRELIMINARY PERFORMANCE RESULTS FROM A ZERO
VALENT METAL REACTIVE WALL FOR THE PASSIVE TREATMENT
OF CHLORINATED ORGANIC COMPOUNDS IN GROUNDWATER**

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ABSTRACT

In an effort to improve the cost/performance for treatment of dissolved-phase chlorinated organics in groundwater, the U.S. Air Force demonstrated a zero-valent iron reactive wall at Lowry Air Force Base (AFB), Colorado. Chlorinated aliphatic hydrocarbons (CAHs) are degraded via a reductive dechlorination reaction involving the zero valent iron. Preliminary results indicate that all of the chlorinated species are rapidly degraded to concentrations below their quantitation limits. Reaction kinetics based on these preliminary results appear to be first order, and degradation rate constants are

presented for nine CAHs. Precipitation of iron salts was demonstrated through evaluation of geochemical parameters. Long-term remediation cost is presented and evaluated on the basis of CAH mass removed.

1. INTRODUCTION

CAHs (e.g., trichloroethene [TCE]) are the principal organic contaminants at many Air Force installations. The overall cost to the Air Force for remediating groundwater contaminated with CAHs by traditional pump and treat technology could become prohibitive, since operational costs will be accrued over a period of many years. Previous studies have indicated that CAHs dissolved in groundwater may be effectively degraded *in situ* when placed in contact with a zero-valent metal, such as iron. Several zero-valent iron reactive walls have successfully remediated groundwater in Canada and the United States. This paper discusses preliminary performance results for a zero-valent iron reactive treatment wall that was installed at a site at Lowry AFB to demonstrate the feasibility of this technology for use at other Air Force sites.

2. BACKGROUND

2.1 Description of the Technology

The degradation of CAHs in aqueous solution by zero-valent metals was recognized some time ago, but was not utilized for groundwater remediation until recently. Several authors have reported CAH degradation by using column reactors containing metal,^{1,2} in laboratory studies,³ and in a pilot-scale field demonstration.⁴ The zero-valent metal reactive wall is an *in situ* technology, which does not require the extraction and subsequent treatment of contaminated groundwater. Rather, groundwater contaminated with CAHs flows through granular, zero-valent iron in a trench, which is excavated perpendicular to the axis of groundwater flow (Figure 1). Other metals (e.g., zinc, tin, and palladium) have also been shown to be effective in the degradation of CAHs, but are more costly and potentially toxic.⁵ The volume of groundwater captured and treated can be controlled by using sheet piling "funnel walls" to direct water into the reactive media. This is often referred to as the funnel and gate method. Dissolved CAHs are degraded through a series of less highly chlorinated intermediates^{6,7} to the nonchlorinated saturated and unsaturated analogs. For this demonstration, a reactive wall consisting of a 10-foot wide permeable iron gate flanked on each side by 15-foot long impermeable sheet piling "funnel walls," was installed to a depth of 18 feet below ground surface (bgs) (Figure 2).

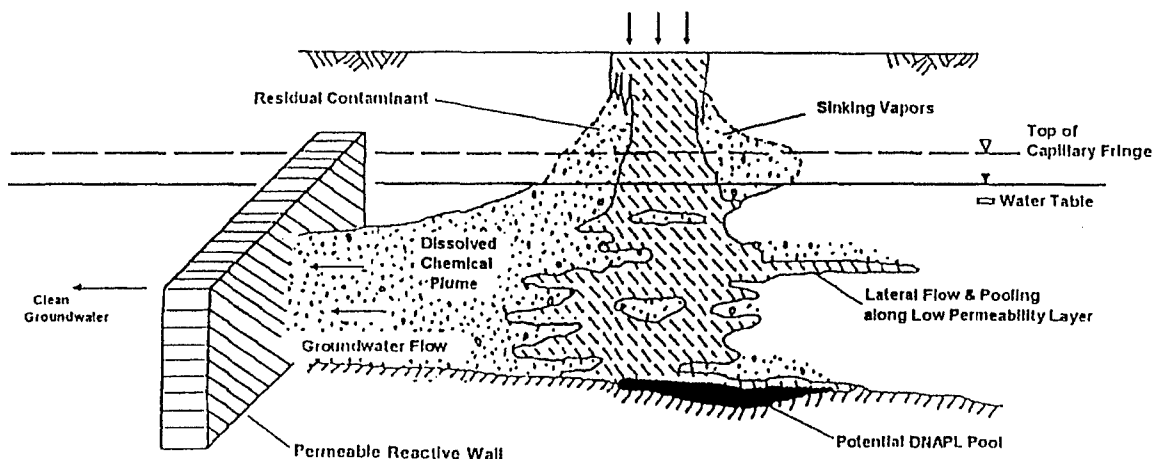


Figure 1. Permeable Reactive Walls (Passive, In Situ)

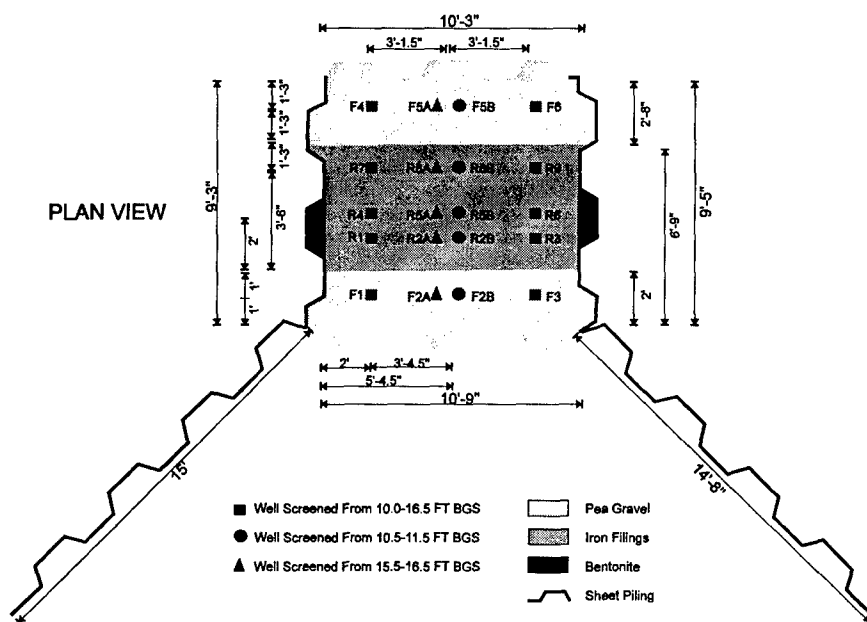


Figure 2. As-Built Treatment Wall Dimensions, Material Composition, and Monitoring Well Locations

In situ zero-valent iron reactive walls have been installed previously and are described in the literature at Canadian Forces Base Borden⁸ and at a commercial electronics manufacturing site in Sunnyvale, California.^{9,10} The Canadian site has the longest operating history of any known site and is reported to have performed without significant change for several years. CAHs present in the groundwater (TCE and perchloroethylene [PCE]) at the site were effectively reduced in concentration after passing through the reactive wall. The commercial electronics site has been in operation for less time and operating results have not been published.

2.1.1 Site Requirements

For the purposes of this demonstration, a major site-selection criterion was the presence of dissolved-phase CAHs at concentrations in excess of 100,000 $\mu\text{g/L}$. These concentrations approximate worst-case conditions for calculating degradation rate constants over a broad range of concentrations. However, site topography, the potential presence of dense, nonaqueous phase liquid (DNAPL), and an adjacent stream precluded installing the reactive wall in the area with highest concentrations of CAHs. Thus, the reactive wall was installed in an area where CAH concentrations were lower (approximately 1,000 $\mu\text{g/L}$) but still significant.

Another requirement was a relatively shallow depth of contamination (less than 30 feet bgs). This reflects depth limitations of the installation techniques planned for use at Lowry AFB. Also, the funnel and gate method is benefited by a confining layer, which prevents contaminated groundwater from flowing under the reactive wall, thus escaping remediation.

2.1.2 Possible Chemical Mechanisms

The successful application of this technology may be dependent on site-specific conditions, which effect the chemical mechanism of the degradation pathway. For example, the buffering capacity of the groundwater may affect reaction rates through the neutralization (or absence) of OH^{-1} produced by oxidation of zero-valent iron with concomitant effects on groundwater pH. Thus, an understanding of the

chemical reaction mechanism is important for the proper evaluation of a prospective site's suitability for remediation by this technology.

Data from a bench-scale column test using groundwater from the Lowry AFB site, as well as other bench scale studies, suggests three possible mechanisms for the reductive dechlorination of CAHs using zero-valent iron—(a) oxidation of Fe^0 to Fe^{+2} , followed by reduction of CAHs by the Fe^{+2} produced; (b) catalytic reduction of CAHs at the metal surface by the H_2 produced from oxidation of Fe^0 to Fe^{+2} ; and (c) direct reduction of CAHs at the metal surface involving the oxidation of Fe^0 to Fe^{+2} with direct transfer of electrons (Figure 3). Matheson and Tratnyek¹¹ and Gillham and O'Hannesin¹² provide a discussion of these mechanisms.

The cell potentials indicated in Figure 3 for individual half cells of each mechanism implies that a significantly reducing environment, as reflected in a negative-redox potential, should be created if any of these mechanisms is operable. The first two mechanisms postulated, reduction by Fe^{+2} and catalytic reduction by H_2 , imply that increases in OH^- concentration could inhibit the reductive dechlorination. The above parameters were studied, and this paper reports data concerning potential mechanisms.

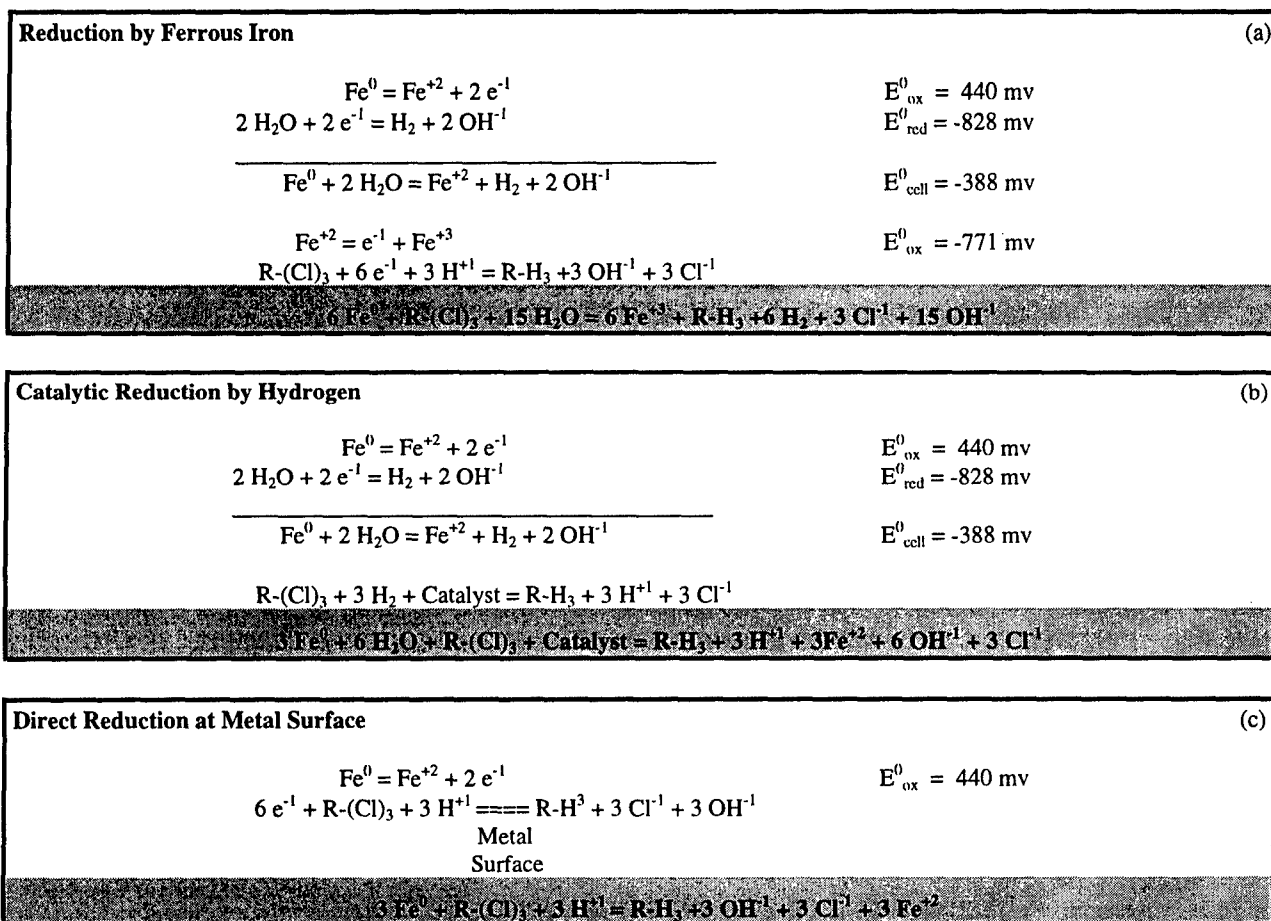


Figure 3. Suggested Chemical Mechanisms for the Reductive Dechlorination of Dissolved-Phase CAHs in the Presence of Iron. (Stoichiometrically Balanced Equations for Degradation of TCE by Each Mechanism are Contained in the Shaded Box.)

2.2 Objectives of the Study

The overall purpose for demonstrating this technology was to assess its usability in similar circumstances at other Air Force installations. The following objectives were identified to support the assessment and implementation of the study:

- Demonstrate effective mass reduction of dissolved CAHs at a lower cost than alternatives, such as pump and treat strategies. Although cost effectiveness is critical to widespread applications, it must be realized that a reactive treatment wall will, if designed properly, degrade toxic CAHs to below quantitation limits, while pump and treat approaches merely transfer CAHs from one media to another and do not eliminate the need for additional effort (i.e., disposal of contaminated carbon or treatment of air stripper vapor-phase effluent).
- Determine first order degradation rate constants. Reliable rate constants are necessary for the design of future cost-effective treatment walls.
- Evaluate precipitation of salts within the wall. Iron (or other) salts could degrade the effectiveness of the wall by impairing groundwater flow, resulting in a reduction of mass CAHs treated or discharge of contaminated groundwater.
- Evaluate end-products produced by reductive dechlorination. A corollary to effective reduction of CAH mass is the production of relatively innocuous by-products. For example, should dechlorination only proceed to the vinyl chloride stage, the solution could be more hazardous than the problem.
- Obtain data to elucidate the mechanism operating to degrade CAHs within the reactive wall.

3. FIELD DEMONSTRATION

The field demonstration was designed to accomplish the aforementioned overall approach and supporting objectives. The field demonstration involved four steps—location characterization, design, construction, and evaluation.

3.1 Location Characterization

The location of the reactive wall was chosen as described in Section 2.1.1, and a site characterization effort was conducted to determine engineering/design parameters for the wall. This effort involved the evaluation of existing regional-scale information; the installation of soil borings and monitoring wells; and provided information on the spatial distribution of hydraulic conductivity, hydraulic potential, excavability, penetrability, and chemistry at the reactive wall location.

The distribution of hydraulic conductivity appeared to be heterogeneous, as evidenced by interbedded sands, silts, and clays observed in the borehole core collected from the alluvial aquifer. Groundwater flow rates across the chosen location were estimated to be approximately 1 foot/day, based on geometric means of existing pump-test data and measured potentiometric gradients. A low permeability claystone (bedrock) underlays the alluvial aquifer at a depth of approximately 17.5 feet bgs. The depth to water was approximately 8 feet bgs at the wall location. The DNAPL source is believed to be located 300 feet upgradient (south) of the wall location.

3.2 Design Approach

The foregoing information was used to determine the design parameters for the reactive wall. Hydraulic conductivity and potentiometric information were numerically modeled to simulate the effects of various wall design scenarios. This iterative process revealed that the design shown in Figure 2 would optimally funnel groundwater through a treatment gate (reactive wall), while avoiding impacts to groundwater or surface water at a nearby stream. Groundwater flow velocities through a gate of this design were predicted to be approximately 2.60 feet/day. This flow rate was used to determine (in part) the thickness of the reactive wall parallel to groundwater flow that would result in the residence time necessary to degrade CAHs to below target concentrations. The required residence time was also determined from degradation rates derived from laboratory column tests conducted on groundwater from the site. This information was also used to design the performance monitoring scheme for the reactive wall. See Figure 2 for the location of the monitoring wells.

3.3 Construction Approach

The construction of the reactive wall involved the use of sealable sheet piling (Waterloo Barrier) driven approximately 18 feet bgs with a crane-mounted hydraulic vibratory hammer. The sheet piling penetrated approximately 6 inches into the low-permeability claystone bedrock. The sheet piling was installed to form a box-shaped gate (reactive wall) with two funnel walls attached. Native material was excavated from the wall using a crane-mounted clamshell; engineered supports were installed to maintain structural integrity of the gate. After excavation, the reactive media (zero-valent granular iron) and various groundwater flow control media (bentonite and 3/8-inch gravel) were emplaced within the wall as shown in Figure 2. Then the sheet piling on the upgradient and downgradient sides of the wall (i.e., gate) were removed to allow groundwater to funnel into and through the reactive iron. Thirty-seven wells and five stream gauges were installed within and around the wall to monitor remedial performance and the influence on surrounding groundwater and surface water flow patterns.

3.4 Evaluation Approach

The performance results of the reactive wall were obtained during the first four months of operation, including a time-zero data point (early December 1995). Performance monitoring involves potentiometric, as well as chemical monitoring. Potentiometric monitoring provided information regarding groundwater flow patterns and variations in these patterns over time. To date, the potentiometric data indicate that flow patterns have been stable and consistent with the numerical modeling predictions.

Chemical monitoring involves the collection and analysis of groundwater samples from the wells shown in Figure 2 and 3 upgradient and 3 downgradient wells not shown in the figure. These wells outside of the wall were screened throughout the saturated zone. All groundwater samples were analyzed for CAHs by Methods SW8010 or SW8260, cations by Method SW6010, anions by Method E300, and field parameters discussed in Section 4. The latter measurements (except alkalinity) were made using a closed-system flow-through cell. Samples for inorganic analyses were obtained using peristaltic pumps with dedicated sampling tubing. Samples for organic analyses were collected using dedicated bailers.

4. RESULTS AND DISCUSSION

4.1 Performance

Concentrations of CAHs were measured in samples taken monthly from the following monitoring wells: upgradient (0 feet); R1, R2, and R3 (1 foot); R3, R4, and R5 (2 feet); and R6, R7, and R8 (3.5 feet). Performance, as measured by the extent of degradation of individual CAHs, was 100 percent in every case and during every sampling event.

4.1.1 Concentration Data

Numerous degradation products of TCE and PCE were present in the groundwater, implying the operation of a dechlorination mechanism *in situ*. TCE was the major component detected during each sampling event, followed by cis-1,2-dichloroethene (DCE). Other CAHs were present at concentrations an order of magnitude lower than TCE and DCE. Table 1 presents concentration data averaged over the first four months of sampling, grouped on the basis of reactive wall cross-sectional distance (i.e., distance from upgradient boundary of wall to sampling point) from which residence times were determined. Figure 4 graphically depicts these data.

TABLE 1. AVERAGE CHLORINATED ALIPHATIC HYDROCARBON CONCENTRATIONS

Wall Cross Section (feet)	TCE	cis-1,2-DCE	trans-1,2-DCE	Vinyl Chloride	1,1-DCE	1,1,1-TCA	PCE	1,1-DCA	1,2-DCA
0	848	221	15.6	24.2	16.3	16.8	13.6	6.56	6.02
1	1.05	10.2	0.23	0.72	0.25	0.17	0.28	0.89	0.49
2	0.18	0.77	0.12	0.47	0.10	0.10	0.25	0.16	0.25
3.5	0.10	0.20	0.10	0.47	0.10	0.10	0.25	0.15	0.25

Note 1: Individual values are averages of monthly averages
Note 2: Non-detect results quantitatively entered as one-half respective quantitation limit

Table 1 indicates that degradation was substantially complete by the time groundwater had flowed 1 foot into the wall (approximately 9 hours residence time). Only cis-1,2-DCE was present at significant concentrations after approximately 9 hours of residence time. By approximately 18 hours of residence time (2 feet into the wall) all analytes had degraded to approximately their respective analytical quantitation limits. The slopes of the concentration curves in Figure 4 are proportional to the first order rate constants. The slowest rates of degradation are for cis-1,2-DCE, 1,1-dichloroethane (DCA), and 1,2-DCA. The results for cis-1,2-DCE, relative to other CAHs, are consistent with the data presented by Gillham.¹³

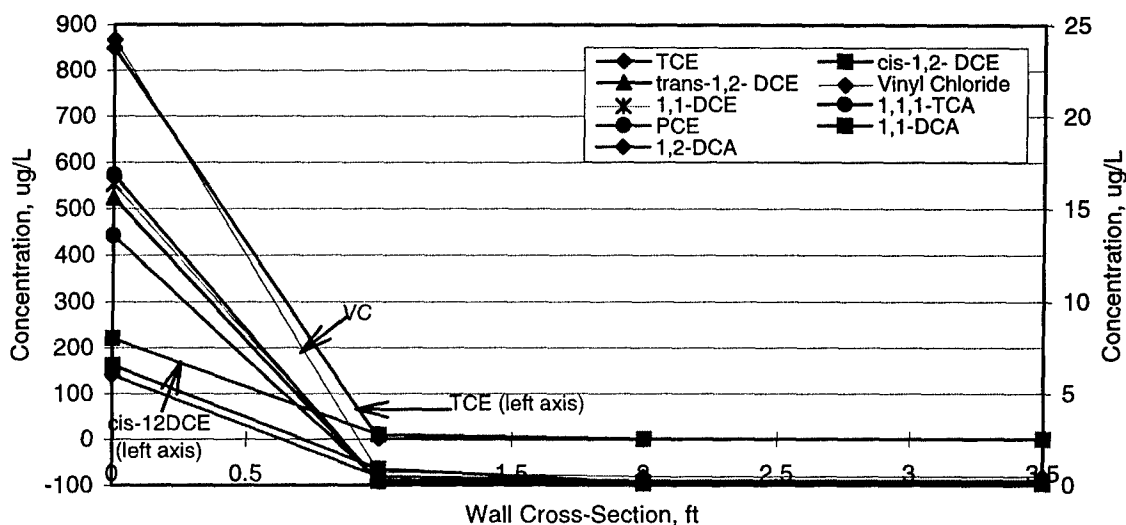


Figure 4. Average (Monthly) Concentrations of Chlorinated Aliphatic Hydrocarbons. Concentrations of TCE and cis-1,2-DCE are on the left axis. Concentrations of all other CAHs are on the right axis.

4.1.2 Calculated Rate Constants

First order rate constants for each CAH were calculated using as C_0 the respective upgradient (0 feet cross section) concentration. Only concentrations determined from samples taken at the 1-foot cross-sectional distance were used for the C_1 concentrations because CAH concentrations in samples taken at greater distances were typically at the detection limit. Reaction time ("t" in the first order rate equation) was estimated by converting the distance (into the wall cross section) to time at a groundwater flow rate of 2.60 feet/day. The resulting rate constants are shown in Table 2. These rate constants (except for TCE and PCE) are conservative because the C_0 values are based on concentrations of CAHs present in upgradient groundwater and do not reflect the additional amounts produced in the wall by reductive dechlorination. Therefore, the actual maximum concentrations existing within the first 1 foot of the wall are unknown (except for TCE and PCE) and may be considerably higher than the upgradient concentrations used as C_0 . When the C_1 concentrations are near the quantitation limit, the actual time required to reach that concentration may not be the "t" determined to the first sampling point. Overestimating "t" would result in underestimating the rate constant.

The monthly average rate constants are based on the concentrations averaged over the three wells present at each wall cross section (i.e., R1, R2, and R3 for the C_1 concentrations). The standard deviations imply that the rate constants and the reductive dechlorination mechanism are not varying significantly over time. The consistency of the rate constants implies that the reactive wall reached chemical equilibrium rapidly. Data presented subsequently reinforces this conclusion. The half lives presented in the table will be useful for designing future reactive walls using 100 percent zero-valent iron.

TABLE 2. AVERAGE¹ FIRST ORDER DEGRADATION RATE CONSTANTS (K, DAY⁻¹)

Sampling Month	TCE	Cis-1,2-DCE	Trans-1,2-DCE	Vinyl Chloride	1,1-DCE	1,1,1-TCA	PCE	1,1-DCA	1,2-DCA
January	16.7	7.94	9.49	10.3	10.5	10.9	8.37	5.04	8.37
February	18.2	8.15	11.9	8.74	10.4	12.9	10.8	5.19	5.43
March	17.7	7.95	12.7	6.98	12.6	13.2	10.8	5.36	5.52
April	17.4	6.91	10.4	6.36	10.5	12.5	10.7	4.75	4.60
Average of Observations	17.5	7.74	11.1	8.08	11.0	12.4	10.2	5.08	5.98
Standard Deviation of "k"	0.61	0.56	1.44	1.76	1.05	1.03	1.20	0.26	1.65
Calc Half Life, Hr	0.9	2.2	1.5	2.1	1.5	1.3	1.6	3.3	2.8
Note 1: Calculated from average of monthly average concentrations									

4.1.3 Degradation End Products

The implication of any of the mechanisms suggested in Figure 3 is the production of less highly chlorinated and more highly saturated hydrocarbons. Evidence of degradation should be accompanied by the appearance of reductive dechlorination end products. Figure 5 illustrates the concentrations of methane, ethane, and ethene in groundwater obtained from one round of sampling (March). Concentrations of ethane and ethene, the proposed end products, reached a maximum at a wall cross-sectional distance of 1 foot. The peak concentrations correlate with the peak CAH degradation activity within the wall, as illustrated in Figure 4. Beyond the 1-foot distance, concentrations of all three gases decrease, indicating a reduction or cessation of their production.

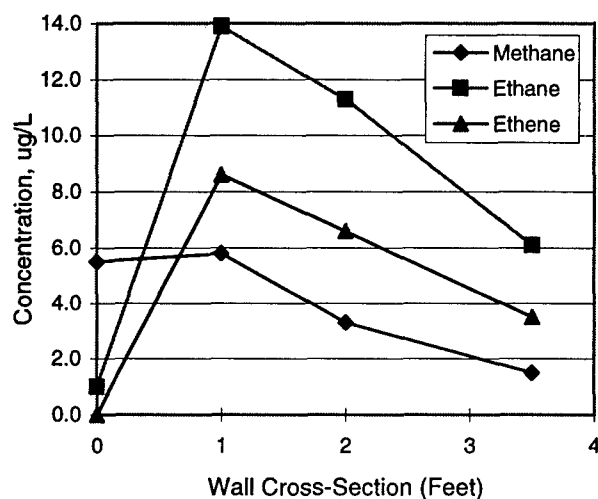


Figure 5. Methane-Ethane-Ethene Concentrations in Groundwater as Function of Cross-Sectional Distance of Wall

Note that methane and a small amount of ethane were present in the upgradient groundwater. This, in addition to the presence of CAH degradation products upgradient from the reactive wall, may indicate that reductive dechlorination occurs within the native aquifer and that methanogenesis is occurring, either as part of or in addition to the degradation. However, reduction of aqueous CO₂ by iron in the aquifer, which can form hydrocarbons, can not be conclusively eliminated as the source of these hydrocarbons.¹⁴

The presence of ethane and ethene may indicate that the reduction of saturated and unsaturated CAHs occurs in parallel (i.e., saturated CAHs go to ethane and unsaturated CAHs go to ethene) or that ethane is the final product of reduction and possibly accumulates in the aquifer.

4.2 Evidence for Mechanism

Based on the mechanisms suggested in Figure 3, the presence of Fe^{+2} , Fe^{+3} , OH^{-1} , and a reducing redox potential might be used to elucidate the mechanism operating for the reductive dechlorination of CAHs. The redox potential of the groundwater flowing through the reactive wall rapidly becomes strongly negative, as illustrated in Figure 6, and presumably reflects the oxidation of Fe^0 to Fe^{+2} . Redox potential results for January are anomalous in light of the degradation already occurring, but subsequent measurements are consistent with the oxidation of iron. However, it is possible that this oxidation is occurring in addition to another degradation mechanism, and these redox potentials do not clearly imply one or another mechanism.

Similarly, the groundwater pH results in Figure 7 seem to reflect the production of OH^{-1} , which is possible by each mechanism in Figure 3, although mechanism "c" (direct reduction at metal surface) does not appear capable of producing sufficient amounts of OH^{-1} to cause such a large elevation of pH. Discussion of alkalinity changes supports the notion that a relatively large quantity of OH^{-1} was produced, thus these data are supportive of mechanisms "a" and "b" and would seem to rule out mechanism "c."

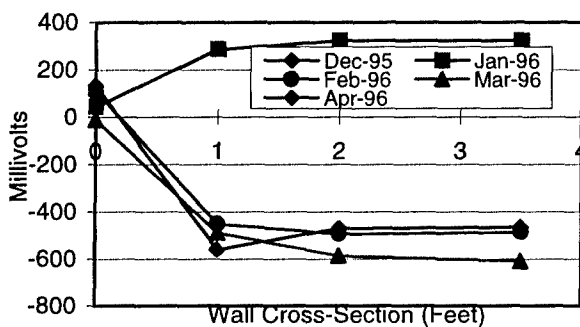


Figure 6. Redox Potential in Groundwater as Function of Wall Cross-Sectional Distance;
Dec 95 = 94 mv

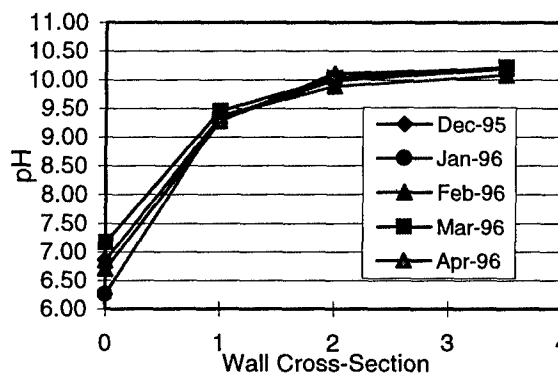


Figure 7. Groundwater pH as Function of Wall Cross-Sectional Distance;
Dec 95 pH = 6.86

4.3 Precipitation

Precipitation has been shown to occur (pilot study results) as a result of the insolubility of certain iron salts at the pH and redox potential existing in the reactive wall. Total alkalinity decreased rapidly with cross-sectional distance into the wall during every sampling event (Figure 8). The total alkalinity upgradient of the reactive wall exists as bicarbonate (HCO_3^{-1}), as expected for groundwater with a near-neutral pH (Figure 9). Bicarbonate concentrations rapidly decline as a function of wall cross section, due to the increasing groundwater pH which shifts the CO_2 equilibrium from the HCO_3^{-1} species to carbonate (CO_3^{-2}). However, CO_3^{-2} is rapidly lost, as illustrated in Figure 10, presumably due to its precipitation as FeCO_3 and possibly $\text{Fe}_2(\text{CO}_3)_3$. This corresponds to approximately 5.9 mmol/L of CO_3^{-1} species lost, which means that a total of approximately 6.2 mmol/L (105 mg/L) of OH^{-1} were produced, most of which neutralized HCO_3^{-1} and very little of which remained to contribute to the Total Alkalinity

downgradient of the 1-foot wall cross section (Figure 11). As previously mentioned, it is difficult to reconcile this quantity of OH^- being produced by mechanism "c" (Figure 3). In addition, both calcium ion and sulfate ion concentrations in groundwater were significantly reduced as groundwater encountered the highly reducing and alkaline conditions within the reactive wall, adding to the precipitation occurring within the wall.

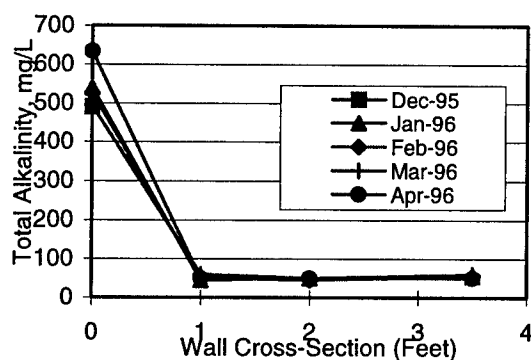


Figure 8. Groundwater Total Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 490 mg/L

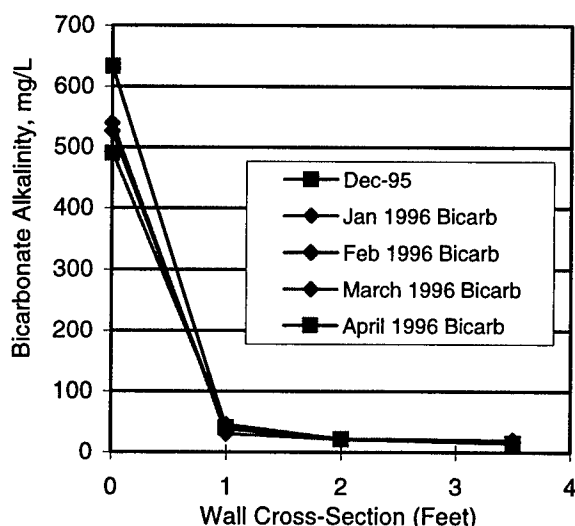


Figure 9. Groundwater Bicarbonate Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 490 mg/L

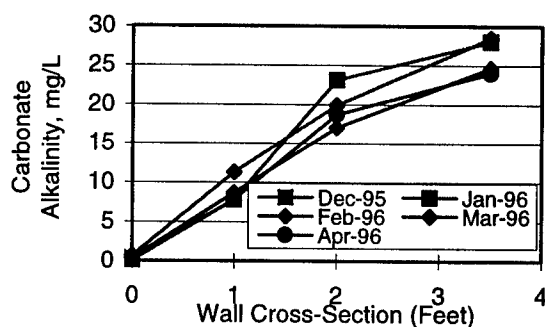


Figure 10. Groundwater Carbonate Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 0

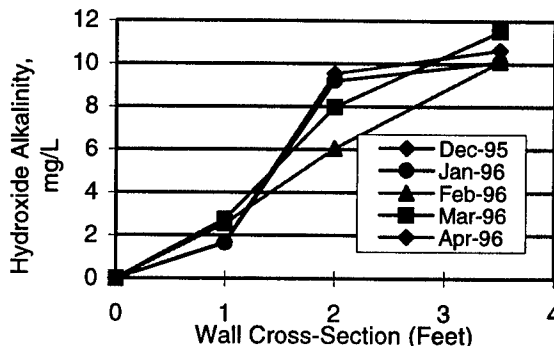


Figure 11. Groundwater Hydroxide Alkalinity as Function of Wall Cross-Sectional Distance; Dec 95 = 0

The presence of Fe^{+3} would imply that reductive dechlorination occurs by oxidation of Fe^{+2} in solution to Fe^{+3} . Due to the precipitation of iron salts, Fe^{+2} and Fe^{+3} were not detected at concentrations greater than 1 mg/L.

5. COST EVALUATION

An integral part of this study is to evaluate and compare the costs of remediation using this technology with other remedial techniques. The cost of this demonstration was high because of the conservative oversize of the wall and the intensive sampling and analysis program needed to evaluate the

performance. Using this technology routinely, will not require such intensive sampling or analysis, lowering costs compared to the demonstration reported in Figure 12.

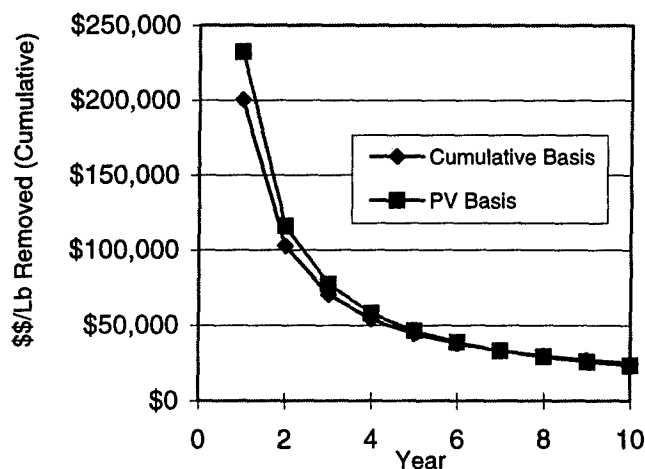


Figure 12. Average Treatment Cost

Figure 12 illustrates the cost per pound of CAH removed for a 10-year time horizon. It was assumed that concentrations and degradation rates and analytical costs are constant over time. It also was assumed that iron replacement was not required during this period. Costs were determined as both the present value and cumulative current costs. Because most of the cost is incurred early (i.e., for installation), the present value and cumulative current costs do not differ very much. The cost of this method approaches \$24,000 per pound of CAH removed (Figure 12). This cost can be expected to be significantly lower as design criteria are further refined for full-scale remediation.

6. CONCLUSIONS

The evidence presented indicates that the zero-valent iron reactive wall is actively degrading CAHs dissolved in groundwater. Degradation is complete and relatively rapid and results in the formation of both ethane and ethene as possible end-products of the degradation. First order rate constants were calculated based on the known upgradient concentrations for each CAH detected. These rate constants are probably conservative in that they may not represent the highest (C_0) concentration of the individual compound, and the actual time for complete degradation of many CAHs is only estimated (based on the time required for groundwater to travel to the monitoring well).

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